



Ethanol steam reforming in a membrane reactor with Pt-impregnated Knudsen membranes

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ABSTRACT

An ethanol reforming membrane reactor (ERMR) with Pt-impregnated Knudsen membranes was investigated to achieve the improvement of ethanol conversion and hydrogen yield. The prepared Pt-impregnated membranes have high permeabilities and reaction activities for the water-gas shift (WGS) reaction. The ethanol reforming-membrane reactor showed ethanol conversion improvement of 7.4–14.4% in comparison with a conventional reactor (CR). Hydrogen yield improvement of 4.2–10.5% was also observed in ERMR with Pt-impregnated SKM in whole reaction temperature range. In addition, CO concentration was considerably reduced via water-gas shift reaction during the permeation.

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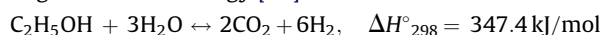
1. Introduction

Hydrogen is considered to be the energy carrier of the future and could have an important role in reducing environmental emissions, but today near to 95% of hydrogen is produced from fossil-based materials such as methane and naphtha [1].

In order to support hydrogen economy, renewable and clean energy source for hydrogen production is demanded. Bio-ethanol is considered as a promising source of hydrogen since it can be produced renewably from several biomass sources such as waste materials from agroindustries or forest residue materials [2]. The bio-ethanol to hydrogen system has the significant advantage of being nearly CO₂ neutral, since the carbon dioxide produced is consumed for biomass growth, thus offering a nearly closed carbon loop [3]. In addition, ethanol is relatively high hydrogen contents, non-toxic, safe and easy to transport.

One of the attractive methods to produce H₂ for processing of bio-ethanol is a catalytic steam reforming reaction, because this reaction is entirely feasible from a thermodynamic point of view [4–6]. Steam reforming of ethanol has been extensively studied over Pd, Ru, Pt, Rh, Co and Ni catalysts supported by various oxide groups [7–16], but its efficiency such as ethanol conversion and

hydrogen selectivity is relatively low in comparison with steam reforming of methanol and dimethyl ether. Ethanol steam reforming process is highly endothermic and requires providing huge amount of energy [17]



Meanwhile, if the membrane reactor system is employed for the ethanol reforming as a hydrogen generator for PEMFC, three important aims should be achieved, which are improvement in ethanol conversion via an equilibrium shift, high hydrogen recovery and effective CO removal. However, in membrane reactor system for hydrogen production, dense and microporous membranes such as palladium alloy and microporous silica membranes have been generally used, which results in low hydrogen recovery due to relatively low permeability. In this reason, Knudsen membrane reactor combined with water-gas shift (WGS) reaction in permeate side has been investigated for methanol and DME steam reforming in our previous work [18–21].

In this work, we have employed an ethanol reforming-membrane reactor (ERMR) with Pt-impregnated Knudsen membranes with high permeability prepared by simple modification of porous stainless steel substrates with colloidal sol of 100 nm in particle diameter and Pt impregnation in order to achieve important aims such as ethanol conversion improvement, high hydrogen yield and CO reduction in one process.

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2. Experimental

2.1. Preparation of composite membranes

2.1.1. Sol synthesis

Colloidal silica sol with 100 nm in particle size was synthesized from base-catalyzed hydrolysis and condensation reaction of tetraethyl orthosilicate (TEOS) purchased from Aldrich. A molar ratio of TEOS, water, ammonia and ethanol was 1:53.6:0.64:40.1. A TEOS/ethanol mixture was stirred vigorously in an oil bath of 50 °C and then an ammonia/water mixture was added. The addition of the ammonia/water mixture was carried out dropwise into the TEOS/ethanol mixture, followed by refluxing the mixture for 3 h with vigorous stirring resulting in stable colloidal silica sol of 100 nm in particle diameter.

2.1.2. Modification of supports

A porous stainless steel (SUS 316L) disk purchased from Mott Metallurgical with average pore size of 0.5 μm , area of 5 cm^2 and thickness of 1 mm was used as the support of Knudsen membranes. The support has wide pore size distribution, rough surface and too many macropores to be used directly. To reduce the pore size and narrow the pore distribution, the support was modified with the silica sol of 100 nm by means of a dipping–rolling–freezing–fast drying (DRFF) and soaking–rolling–freezing–fast drying (SRFF) method reported in our previous publication [22]. It was confirmed that the freezing step of the DRFF and SRFF method was most important to obtain a crack-free silica layer. The modified porous stainless steel has Knudsen permeation properties with remarkably high gas permeance. This membrane is designated as the stainless steel-supported Knudsen membrane (SKM).

2.1.3. Pt-impregnated composite membranes

In order to induce surface diffusion of hydrogen and WGS reaction inside the membrane, stainless steel-supported Knudsen

membranes (SKM) were impregnated with tetraammine platinum (II) hydroxide hydrate (TPH) precursor purchased from Aldrich. In a typical preparation, to eliminate moisture in inner pore, the SKM was dried at 70 °C for 3 h under vacuum. And then SKM was immersed in 20 mL of 1.5 wt% TPH aqueous solution for 3 min. Afterward, TPH infiltrated SKM was dried at 70 °C overnight, and calcined at 500 °C for 2 h.

2.2. Membrane reactor tests

Fig. 1 shows the schematic diagram of membrane reactor for ethanol steam reforming. For all tests of ethanol reforming, 1 g of Rh–SiO₂ catalysts was used. Rh–SiO₂ catalyst was synthesized by non-surfactant templating method reported in our previous work [23]. Before a reaction test, the catalysts were reduced in a hydrogen flow (70 mL/min) at 200 °C for 60 min. The whole ethanol reforming tests were conducted in a reaction temperature range from 300 °C to 600 °C. The H₂O/EtOH mixture with a molar ratio of 5 was fed at a liquid feed flow rate of 0.03 mL/min. The H₂O/EtOH mixture was vaporized by a preheating line, and diluted by argon carrier gas with a flow rate of 70 mL/min. A flow rate of argon sweeping gas in a permeate side was 100 mL/min. The concentrations of reactants and products in the retentate and permeate sides were analyzed by using a gas chromatograph (DS 6200, Donam Inc., Korea) equipped with Porapack T column and thermal conductivity detector. The flow rate of the gases was measured by using a soap film flow meter. In a membrane reactor, the ethanol conversion, hydrogen selectivity and hydrogen yield were calculated by following equations:

Ethanol conversion (%)

$$= \frac{\text{Ethanol}_{\text{feed}} - \text{Ethanol}_{\text{retentate}} - \text{Ethanol}_{\text{permeate}}}{\text{Ethanol}_{\text{feed}}} \times 100$$

$$\text{Hydrogen selectivity (\%)} = \frac{1}{6} \times \frac{\text{Mole of produced hydrogen}}{\text{Mole of reacted Ethanol}}$$

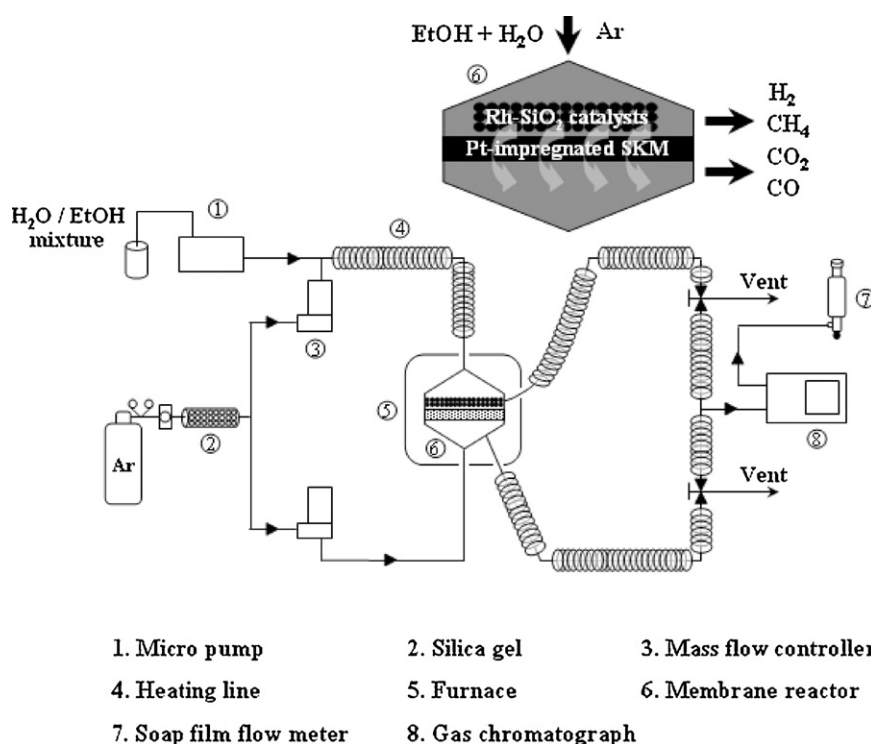


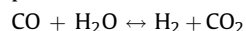
Fig. 1. Schematic diagram of ethanol reforming-membrane reactor.

$$\text{Hydrogen yield (\%)} = (\text{Hydrogen selectivity} \times \text{Ethanol conversion}) \times \frac{1}{100}$$

To confirm improvement of ethanol conversion and hydrogen yield in membrane reactor system, ethanol steam reforming in a conventional reactor (CR) was also conducted by replacing the Knudsen membrane in the membrane reactor by a non-porous stainless steel disk. In order to improve ethanol conversion and hydrogen yield, the SKM and Pt-impregnated SKM were employed in the ethanol reforming-membrane reactor. To investigate the effect of Pt impregnation in SKM, the ethanol reforming efficiency of ERM with the Pt-impregnated SKM was compared with that of ERM with the SKM. Preliminary to the reactor test, the membranes were reduced in a hydrogen flow at 200 °C for 60 min.

2.3. Permeation and WGS reaction tests for membranes

In order to confirm the permeation behavior for reactants and products of ethanol reforming, permeation test was carried out for a single component of H₂O, EtOH, CO₂ and H₂ by means of a sweeping gas method at 300–500 °C. In ethanol steam reforming, CO can be produced as an intermediate product which is subsequently converted into CO₂ by the WGS reaction. To observe the WGS reaction during permeation through the membranes, CO₂ production rate of the SKM and Pt-impregnated SKM was observed by permeation of CO and water vapor without catalysts at 300–600 °C. The production rate of CO₂ is the same as hydrogen production rate stoichiometrically



For permeation and WGS reaction tests, liquid and gas were fed at a flow rate of 0.03 mL/min and 70 mL/min and concentration of permeated liquid and gas was analyzed by a gas chromatograph.

For permeation tests, permeance (F_i [mol/m² s Pa]) of gas of i components penetrating through the membrane is defined as

$$F_i = \frac{Q_i}{A(P_{f,i} - P_{p,i})} = \frac{J_i}{\Delta P_i}$$

where Q_i is the permeation quantity [mol/s], A is the permeation area of membranes [m²], $P_{f,i}$, $P_{p,i}$ was partial pressure for i components in the feed side and the permeation side.

3. Results and discussion

The improvement of the reaction efficiency for ethanol reforming such as ethanol conversion and hydrogen yield through the ethanol reforming-membrane reactor system has been reported. Ethanol reforming in a conventional reactor, ERM with SKM and ERM with Pt-impregnated SKM were conducted. Ethanol steam reforming is an endothermic reaction that produces hydrogen and carbon dioxide if ethanol reacts in the most desirable way. However, by-products such as carbon monoxide, methane, acetaldehyde and ethylene may be formed through several reaction pathways [1]. In order to maximize hydrogen production, it is crucial to ensure sufficient supply of steam and minimize ethanol dehydration and decomposition [12]. The acetaldehyde, formed by dehydrogenation of the ethanol, is easily decarbonylated by the Rh to form CH₄ and CO, while ethylene, produced by the dehydration, is converted to C1 by steam reforming. For Rh contained catalysts, acetaldehyde and ethylene are almost converted into C1 in the presence of excess water [24]. In our reaction conditions, intermediate products such as acetaldehyde and ethylene were not detected due to high H₂O/EtOH molar ratio.

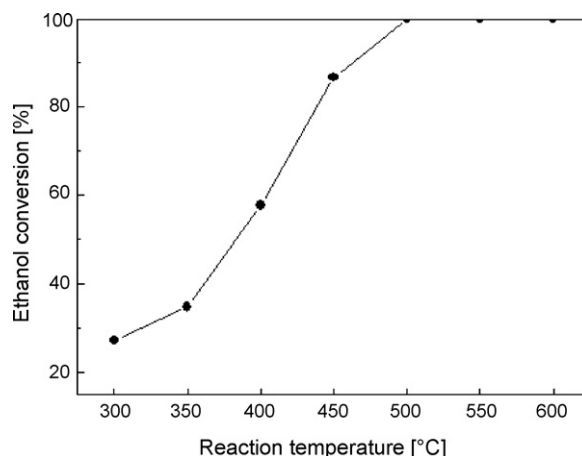


Fig. 2. Ethanol conversion with different reaction temperatures in a CR.

3.1. Ethanol steam reforming in a conventional reactor

H₂, CH₄, CO₂ and CO were produced as main products. H₂ and CO₂ are dominantly produced by steam reforming of intermediate product methane and WGS reaction of intermediate product CO [1]. Fig. 2 shows the ethanol conversion in a CR with different reaction temperature. Ethanol conversion in a CR was about 28% at 300 °C and around 100% above 500 °C. Fig. 3 exhibits concentration of products in a CR. Hydrogen concentration was increased with increasing temperature and the maximum concentration was 62% at 600 °C. Concentration of methane was decreased with increasing temperature due to methane steam reforming at high temperature. Concentration of CO was 50% at 300 °C and decreased with increasing reaction temperature by sufficient steam supply.

3.2. Ethanol steam reforming in a membrane reactor with SKM

Fig. 4 shows the concentration of products in an ERM with SKM in retentate (a) and permeate (b) sides. Concentration of products in an ERM with SKM shows similar profile to a CR. Hydrogen concentration was increased with increasing temperature due to methane steam reforming and WGS reaction and the maximum hydrogen concentration was 62% at 600 °C. Fig. 5 exhibits ethanol conversion for different reactor configurations with different reaction temperature. Compared to a CR, the ethanol conversion in the ERM with SKM was decreased below 500 °C.

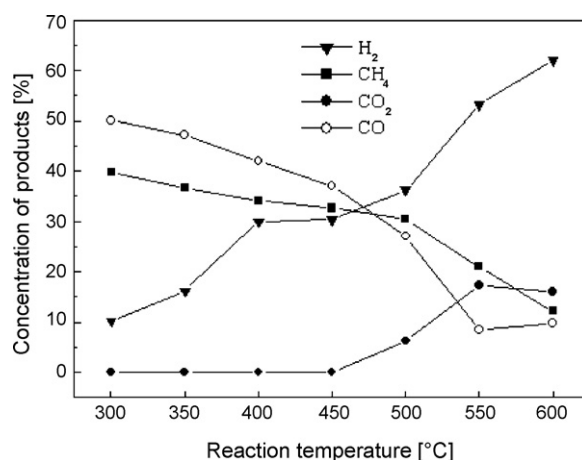


Fig. 3. Concentration of products with different reaction temperatures in a CR.

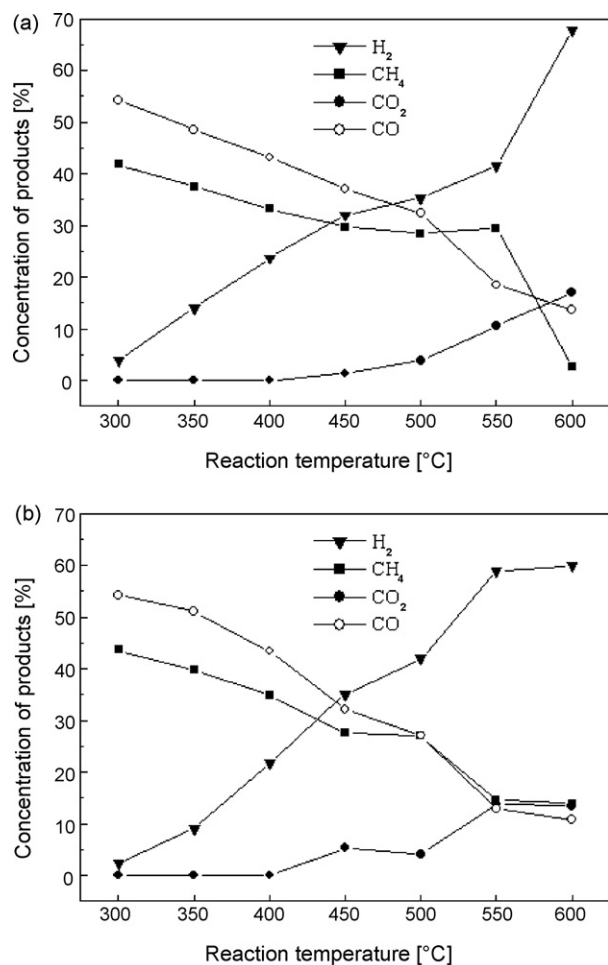


Fig. 4. Concentration of products with different reaction temperatures in an ERMR with SKM in (a) retentate and (b) permeate sides.

More details on decrease in ethanol conversion in ERMR with SKM were described in Section 3.3.

3.3. Ethanol steam reforming in a membrane reactor with Pt-impregnated SKM

As shown in Fig. 5, in case of the ERMR with SKM, improvement of ethanol conversion was not observed in comparison with the CR. However, in case of ERMR with Pt-impregnated SKM, ethanol conversion improvement of 7.4–14.4% was observed in whole reaction temperature range. In our previous publication [18], the total permeance difference (TPD = \sum permeance of products – \sum permeance of reactants) was defined as a factor of membrane performance and investigated relationship between the TPD and reaction conversion. The higher TPD value resulted in the higher improvement of reaction conversion. Table 1 shows the TPD value of the membranes at 300–500 °C. For the SKM, TPD of 2.03×10^{-8} to 3.57×10^{-8} was observed. On the other hand, for the Pt-impregnated SKM, TPD of 1.09×10^{-7} to 1.29×10^{-7} was observed. It is considered that the relatively low ethanol conversion of ERMR with SKM was caused by the low TPD value of the SKM which is derived from relatively high water vapor permeance. In order to study the effect of Pt-impregnated SKM on reaction conversion with different reaction temperature, an

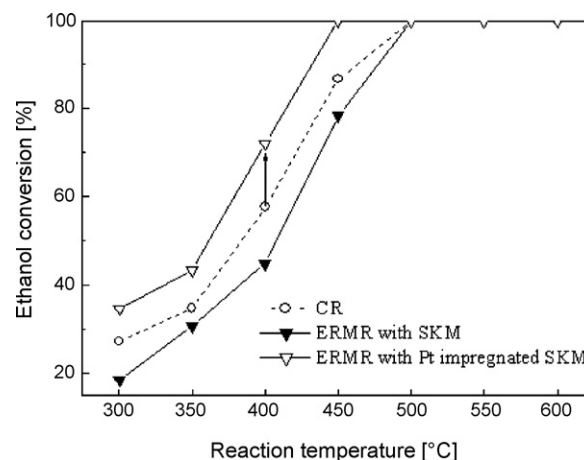


Fig. 5. Ethanol conversion with different reaction temperatures in different reactor configurations.

Table 1

Total permeance difference (TPD) of the membranes with temperature

Type of membrane	TPD (mol/m ² s Pa)		
	300 °C	400 °C	500 °C
SKM ($\times 10^{-8}$)	2.03	3.57	2.65
Pt-impregnated SKM ($\times 10^{-7}$)	1.29	1.11	1.09

Arrhenius plot was observed in the temperature range of 300–450 °C. Fig. 6 exhibits Arrhenius plot of ethanol conversion with different reaction temperature in a CR and ERMR with Pt-impregnated SKM. For the CR and ERMR with Pt-impregnated SKM, a little change of the slope, corresponding to the activation energy, was observed. This is because the significant change of TPD value with temperature was not observed for the ERMR with Pt-impregnated SKM (Table 1). The higher TPD leads to the higher extent of conversion improvement [18]. In other words, independence of the TPD on temperature as shown in Table 1 resulted in nearly constant improvement of conversion in the temperature range of 300–450 °C. Therefore, the activation energy of the ERMR with Pt-impregnated SKM was similar to that of the conventional

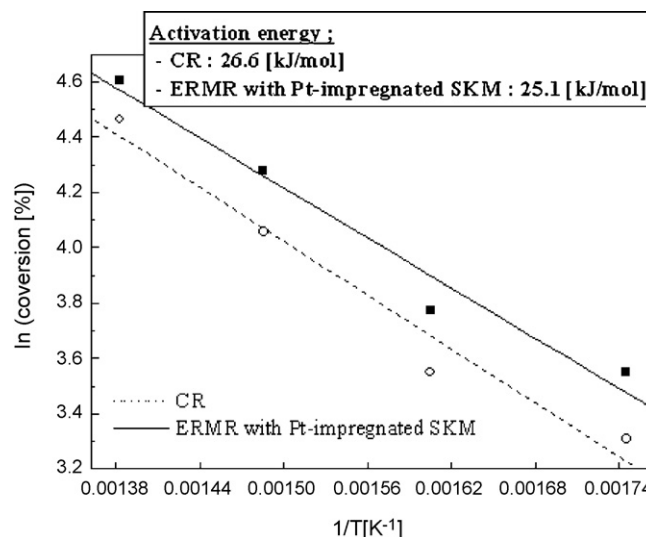


Fig. 6. An Arrhenius diagram of ethanol conversion for a CR and ERMR with Pt-impregnated SKM.

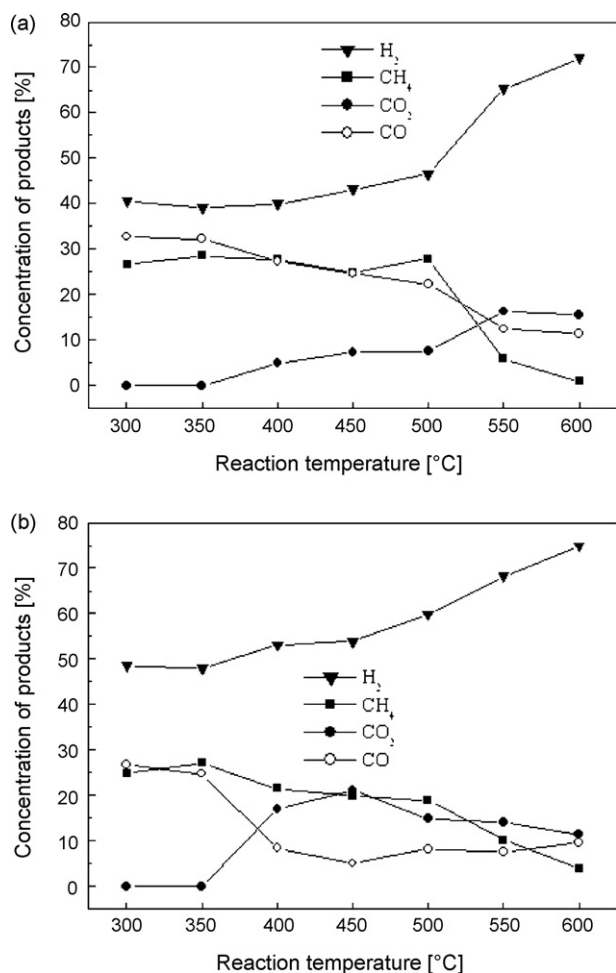


Fig. 7. Concentration of products with different reaction temperatures in an ERMR with Pt-impregnated SKM in (a) retentate and (b) permeate sides.

reactor. Fig. 7 shows the concentration of products in ERMR with Pt-impregnated SKM in retentate (a) and permeate (b) sides. Compared with CR and ERMR with SKM, hydrogen concentration increased in whole reaction temperature range and increased with increasing temperature. Concentration of hydrogen increased by 33% in comparison with CR at 300 °C. Compared to permeate side of ERMR with SKM in Fig. 4(b), CO concentration of permeate side for ERMR with Pt-impregnated SKM in Fig. 7(b) was significantly decreased in the temperature range of 400–500 °C and hydrogen concentration was increased. In particular, compared to conventional reactor, CO concentration remarkably decreased from 37% to 5.1% at 450 °C. Effect of Pt-impregnated SKM on WGS reaction was described in following section. To evaluate the reactor performance, an important parameter to be considered is the hydrogen yield. Fig. 8 presents hydrogen yield for the ethanol reforming in CR, ERMR with SKM and ERMR with Pt-impregnated SKM. Compared to CR, ERMR with SKM did not show improvement in hydrogen yield. In contrast, hydrogen yield of ERMR with Pt-impregnated SKM was much higher than that of the CR. Hydrogen yield improvement of 4.2–10.5% was observed.

3.4. Effect of Pt-impregnated composite membranes on WGS reaction and permeation behavior

The WGS reaction is an important step to diminish CO concentration and to produce additional hydrogen in ethanol

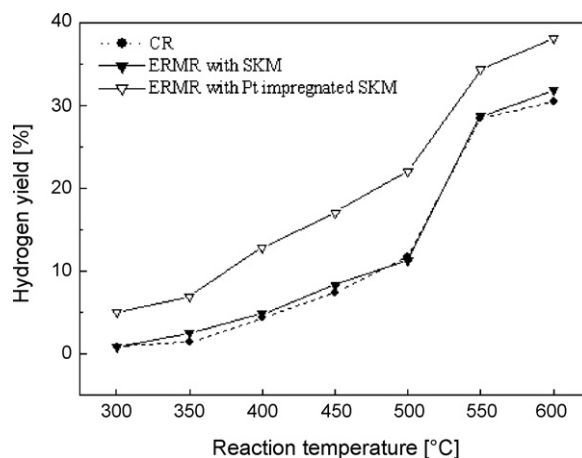


Fig. 8. Hydrogen yield with different reaction temperatures in CR, ERMR with SKM and Pt-impregnated SKM.

reforming process. During permeation through the Pt-impregnated SKM, permeating CO is converted to CO₂ and H₂ through the reaction with permeating water-vapor. Fig. 9 exhibits CO₂ production rate of the SKM and Pt-impregnated SKM by permeation of CO and water vapor without catalysts. Both the SKM and Pt-impregnated SKM showed activity for the WGS reaction. Presumably, it is considered that the silica particles inside pore of the membranes have activity for the WGS reaction. Especially, the Pt-impregnated SKM has higher CO₂ production rate than that of the SKM. At the permeation temperature of 500 °C, CO₂ production rate was 5.0×10^{-6} mol/min. The CO₂ production rate increased by 500 °C and decreased at reaction temperature of 600 °C. Permeation behavior of the membranes influences the performance of membrane reactor during the reaction. However, it is difficult to measure permeance of products and reactants during the reaction because of WGS reaction through the membranes. Therefore, permeation tests were conducted by using a single gas and vapor for H₂, CO₂, EtOH and H₂O. Fig. 10 shows permeances of H₂, CO₂ (a) and EtOH, H₂O (b) for the SKM and Pt-impregnated SKM with different permeation temperature. Ethanol was not detected in permeate side for the SKM and Pt-impregnated SKM. As shown in Fig. 10(a), after Pt-impregnation on the membrane, permeances of H₂ and CO₂ were not decreased in whole reaction temperature range, whereas H₂O permeance was decreased in Fig. 10(b). It is considered that the Pt-impregnation in silica composite membranes contributed to the surface diffusion for H₂ and CO₂ on Pt

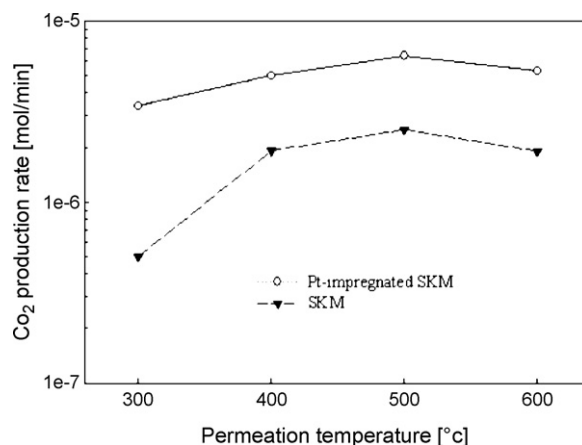


Fig. 9. CO₂ production rate for the SKM and Pt-impregnated SKM.

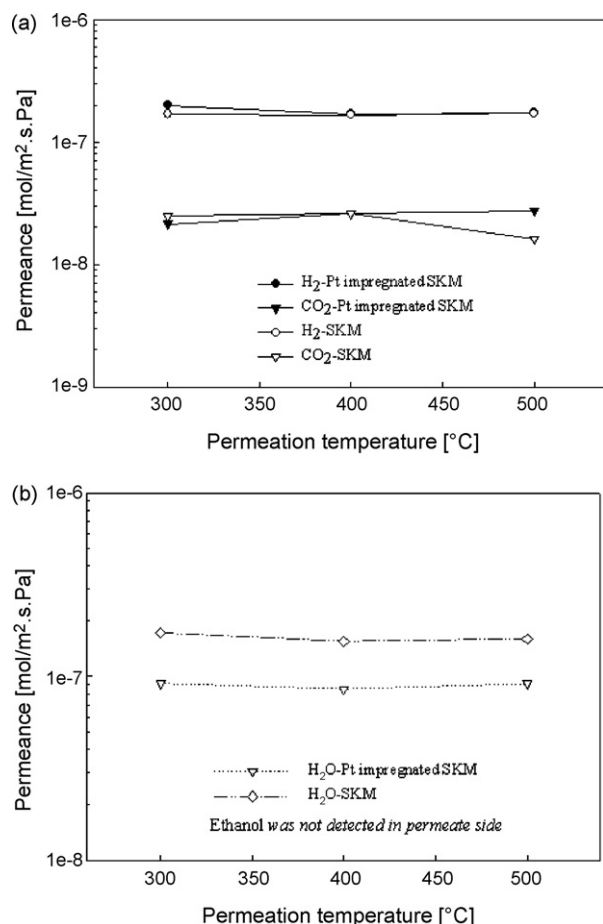


Fig. 10. Permeance of H₂, CO₂ (a) and EtOH, H₂O (b) for the SKM and Pt-impregnated SKM with different permeation temperatures.

particle. The improvement of reaction conversion through the membrane reactor system is derived from dominant permeation of products compared to reactants [18]. As shown in Fig. 9, it is confirmed that the water-vapor permeance decreased after Pt-impregnation inside the membranes while the H₂ and CO₂ permeance showed a little change. In other words, the permeance of the reactant for ethanol reforming decreased, and the permeance difference between reactants and products of the ethanol reforming became larger after Pt-impregnation inside the membranes. Therefore, in the case of ERMR with Pt-impregnated SKM, the ethanol conversion and hydrogen yield were significantly

improved via promotion of equilibrium shift after the Pt-impregnation inside the membranes. In summary, the ethanol conversion and hydrogen yield improvement were simultaneously achieved through the membrane reactor with Pt-impregnated SKM. Moreover, CO concentration was remarkably reduced through the membranes without additional process.

4. Conclusions

Ethanol steam reforming in an ERMR with Pt-impregnated SKM which have remarkably high permeability and activity for the WGS reaction was investigated. Compared to a conventional reactor, ethanol conversion improvement of 7.4–14.4% and increase in hydrogen yield of 4.2–10.5% were achieved in ERMR with Pt-impregnated SKM. Moreover, CO concentration was remarkably reduced through the membranes without additional process. Compared to conventional reactor, CO concentration decreased from 37% to 5.1% at 450 °C. The improvement of reaction conversion through the membrane reactor system is derived from dominant permeation of products compared to reactants.

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